Ab INITIO CALCULATIONS AND KINETIC MODELING OF HALON AND HALON REPLACEMENTS

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Introduction

The mode of action of the chemical-acting flame suppression agents such as the halons is generally, though not universally, accepted. The details of the several reactions involved in chemical suppression have been studied by many groups using experimental and computational techniques[1]. In this paper we report on the calculation of formation enthalpies for a number of halocarbons used, or proposed for use, in flame suppression. Additional calculations have been completed on the radical species and transition states that are important in describing key reactions of flame suppressants. These data are being used to calculate kinetic rate constants that will be used to improve the detailed description of flame extinguishment. Comparisons of computational and experimental results are given.

Calculations and Results

Ab initio calculations were performed using the Gaussian 92 and 94 codes on Cray X-MP, Cray Y-MP, Cray C90, Convex C3820, SUN-Sparc, HP-PARisk, and SGI Power-Challenge computers[2,3]. Table 1 lists the 69 reactions for which calculations have been completed or are in progress. Some results of these calculations are given below.

Enthalpies of formation for fluoromethanes[4] and chlorofluoromethanes[5], using a variety of *ab initio* methods have been reported. Comparisons between results using the G2, G2(MP2) and CBS-Q methods reveal that all exhibit systematic errors dependent on the number of halogens in the molecule. Figure 1 shows the deviations from experiment for chloromethanes, fluoromethanes, and chlorofluoromethanes. The errors are easily corrected using isodesmic reactions to provide results that compare favorably with experiment. An equivalent process, first employed in the BAC-MP4 method, is the employment of bond additivity corrections (BACs), which also give results in good agreement with experiment. Figure 2 shows the results corrected using BACs, with the BAC-MP4[6] results shown for comparison. Calculations on fluoroethanes also reveal systematic errors as shown in Figure 3. The use of BACs has again been found to correct all results, generally to within experimental error. The corrected formation enthalpies for the three methods used in this study and the BAC-MP4 results are shown in Figure 4.

The ultimate reason for calculation of the formation enthalpies, and the energies of various transition states, is to provide reliable rate equations for reactions for which experimental data are not available. Reactions of species such as hydrogen and hydroxyl radicals with halocarbon molecules have been experimentally studied and they are being used to evaluate the accuracy of computationally derived rate constants. As an example, the reaction of the hydroxyl radical with the hydrochlorofluorocarbon, HCFC 124,

$$CHFCl\text{-}CF_3 + HO\bullet \text{ ------> } \bullet CFCl\text{-}CF_3 + H_2O$$

has been thoroughly modeled. As shown in Figure 5, there is a small activation barrier (8.4 kJ/mol) at the G2(MP2) level of theory. Figure 6 shows the same activation barrier with the potential energy surface calculated as a function of the dihedral angles that define the positions of the CF_3 rotor and the O-H group.

Rate constants for the forward and reverse reactions are being calculated using canonical variational transition state theory with zero-curvature tunneling as implemented in POLYRATE. In addition to the the energies, moments of inertia and vibrational frequencies for reactants, products, and transition states were obtained from the *ab initio* calculations. The results of these calculations are given in Figure 7. It is noted that such excellent agreement with experiment is not guaranteed. Thus, an active part of our research is defining the minimum size of the basis set and the level of electron correlation necessary for reliable results. It has been found that low energy vibrational frequencies are a significant source of error, so attention is being given to maximize the reliability of those calculations. Additional corrections necessary to provide the requisite level of fidelity to experiment are also being explored.

The reactions of other HCFCs with OH radicals have also been studied, as have various reactions of FCs, HFCs, and bromo- and iodo-methanes. Following are results of some of the studies.

The pyrolysis of CH_3X results in a dehydrohalogenation reaction to give methene and hydrogen halide in the cases where X = F and Cl. When X = I, an elimination reaction yields the methyl radical plus the iodine atom. When X = Br, the elimination reaction also appears to be favored. The reaction of iodomethane with the hydrogen atom was found to prefer the abstraction of HI, rather than the removal of H_2, in agreement with experiment. (See Figure 8) The reaction of oxygen atoms with CH_3I resulting in the formation of OI was found to occur without a barrier, other than the exothermicity of the reaction. This reaction, too, showed good agreement with experimental results.

The reaction of hydrogen atoms with fluoromethanes has been studied in some detail. Computational results have shown that the dominant reaction pathway is the abstraction of hydrogen, rather than the thermodynamically preferred abstration of fluorine to form hydrogen fluoride. The reaction with CF_4 can proceed only via the slow abstraction of fluorine, so it is not expected to be an important species in flame suppression. That is, it is expected to contribute primarily as a physical flame suppressant. Details of this work will be published shortly.

Conclusion

Thermodynamic descriptors of a large number of reactions have been calculated using multiple *ab initio* protocols. Although some variation between the protocols is observed, it has been shown that the results are generally in excellent agreement with experiment. The rate constants

calculated from the ab initio results show an equally good agreement with experimental results, where available. Conclusions regarding preferred reaction pathways and products drawn from this work have suggested some differences from expected results and indicate the need for additional experimental confirmation.

References and Notes

1. For recent review, see Burgess, D. R. F., Jr.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R.; *Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons, NIST Technical Note 1412*, U. S. Government Printing Office, Washington, 1995.

2. Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

3. The use of Department of Defense high performance computing facilities is acknowledged. (To be modified.)

4. Berry, R. J.; Burgess, D. R. F., Jr.; Nyden, M. R.; Zachariah, M. R.; Schwartz, M., *J. Phys. Chem.*, **1995**, 99, 17145.

5. Berry, R. J.; Burgess, D. R. F., Jr.; Nyden, M. R.; Zachariah, M. R.; Melius, C. F.; Schwartz, M., *J. Phys. Chem.*, **In Press.**

6. (a) Ho, P.; Melius, C. F., *J. Phys. Chem.*, **1990**, 94, 5120. (b) Allendorf, M. D.; Melius, C. F., *J. Phys. Chem.*, **1993**, 97, 72.

Table 1: Reactions of halocarbons being investigated by computational methods.

Reaction Type	CFC Reactants
H abstraction by H ($RH + H\bullet \Rightarrow R\bullet + H_2$)	CH_4, CH_3F, CH_2F_2, CHF_3 CH_3Cl, CH_2Cl_2, $CHCl_3$ CH_3I
Halogen abstraction by H ($RX + H\bullet \rightarrow R\bullet + HX$)	CH_3F, CH_2F_2, CHF_3, CF_4 CH_3Cl CH_3I
H substitution ($RX + H\bullet \rightarrow RH + X\bullet$)	CH_3F, CH_2F_2, CHF_3, CF_4 HCl
H abstraction by OH ($RH + OH\bullet \rightarrow R\bullet + H_2O$)	CH_4, CH_3F, CH_2F_2, CHF_3, HF CH_3Cl, CH_2Cl_2, $CHCl_3$, HCl CHF_2Cl, $CHFCl_2$ CH_3I CH_3CH_2Cl (C_1 & C_2), CH_2ClCH_2Cl CH_3CF_2Cl, CH_3CFCl_2, CH_2ClCF_2Cl, CH_2ClCF_3, $CHCl_2CF_3$, $CHFClCF_3$
H abstraction by O ($RH + O: \rightarrow R\bullet + OH\bullet$)	CH_4, CH_3F, CH_2F_2 CH_3Cl, HCl CH_3I
HX elimination ($RHX \rightarrow R: + HX$)	CH_3F, CH_2F_2, CHF_3 CH_3Br, CH_3I CH3CH2F, CH_2FO, CH_2ClO
H abstraction by a halogen ($RH + X\bullet \rightarrow R\bullet + HX$)	Cl: CH_4, CHF_3, CH_3Cl, H_2O_2 F: H_2O_2
I abstraction by OH ($RX + OH\bullet \rightarrow R\bullet + HOX$)	CH_3I, CF_3I
H ahstraction by CH_3 ($RH + CH_3\bullet \rightarrow R\bullet + CH_4$)	CF_4, CH_3Cl
Miscellaneous Abstraction Reactions	$CH_3Cl + HO_2\bullet \rightarrow CH_2Cl\bullet + H_2O_2$ $ClO\bullet + O: \rightarrow Cl\bullet + O_2$ $HCl + O: \rightarrow Cl\bullet + OH\bullet$ $HCl + Cl\bullet \rightarrow Cl_2 + H\bullet$
Miscellaneous Elimination Reactions	$CH_2ClO\bullet \rightarrow CH_2O + Cl\bullet$ $CH_2ClO\bullet \rightarrow CHClO + H\bullet$

Figure 1: Deviation from Experiment of Formation Enthalpies for Various Halomethanes.

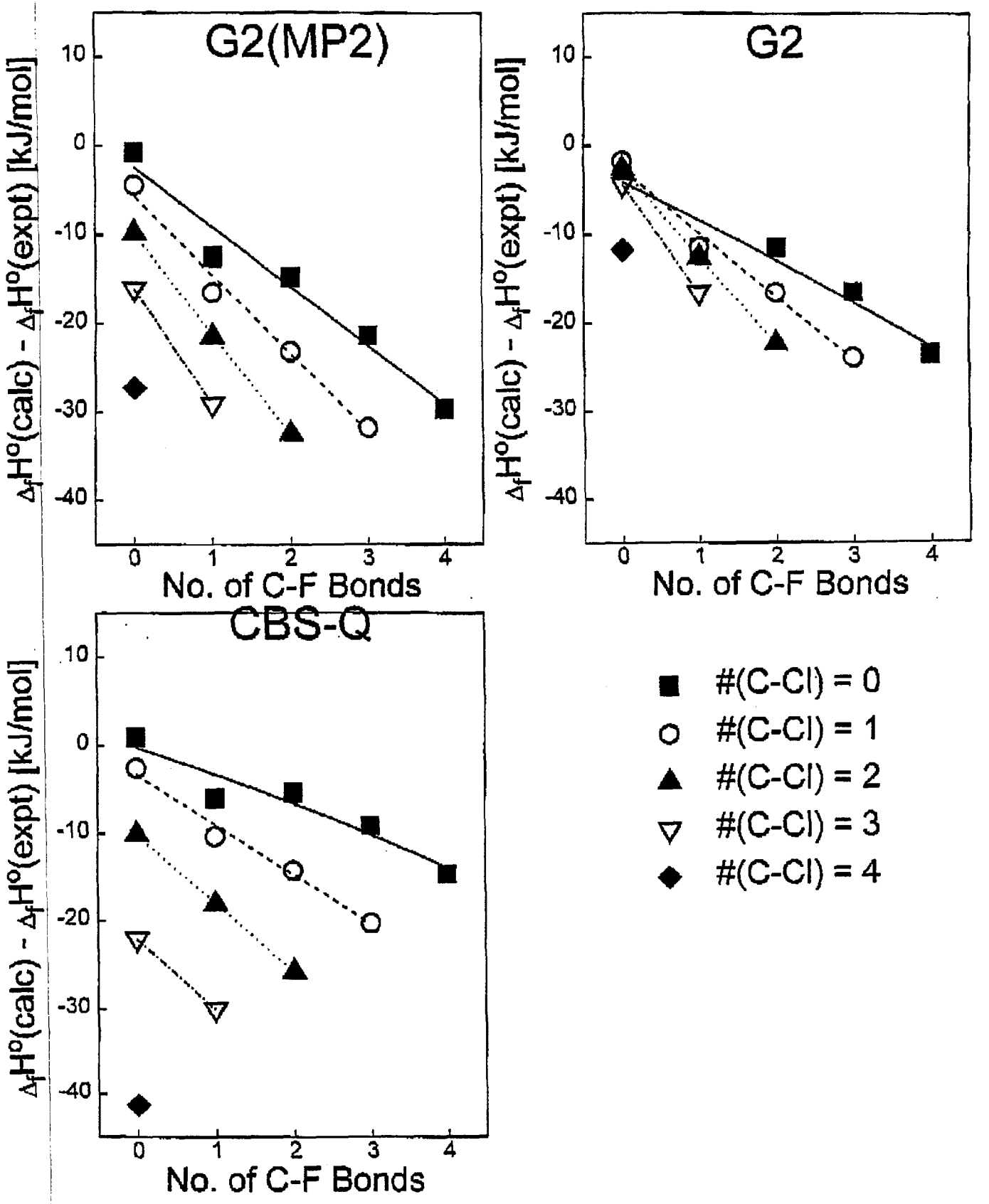

Figure 2: Deviation from Experiment of Corrected Formation Enthalpies for Various Halomethanes.

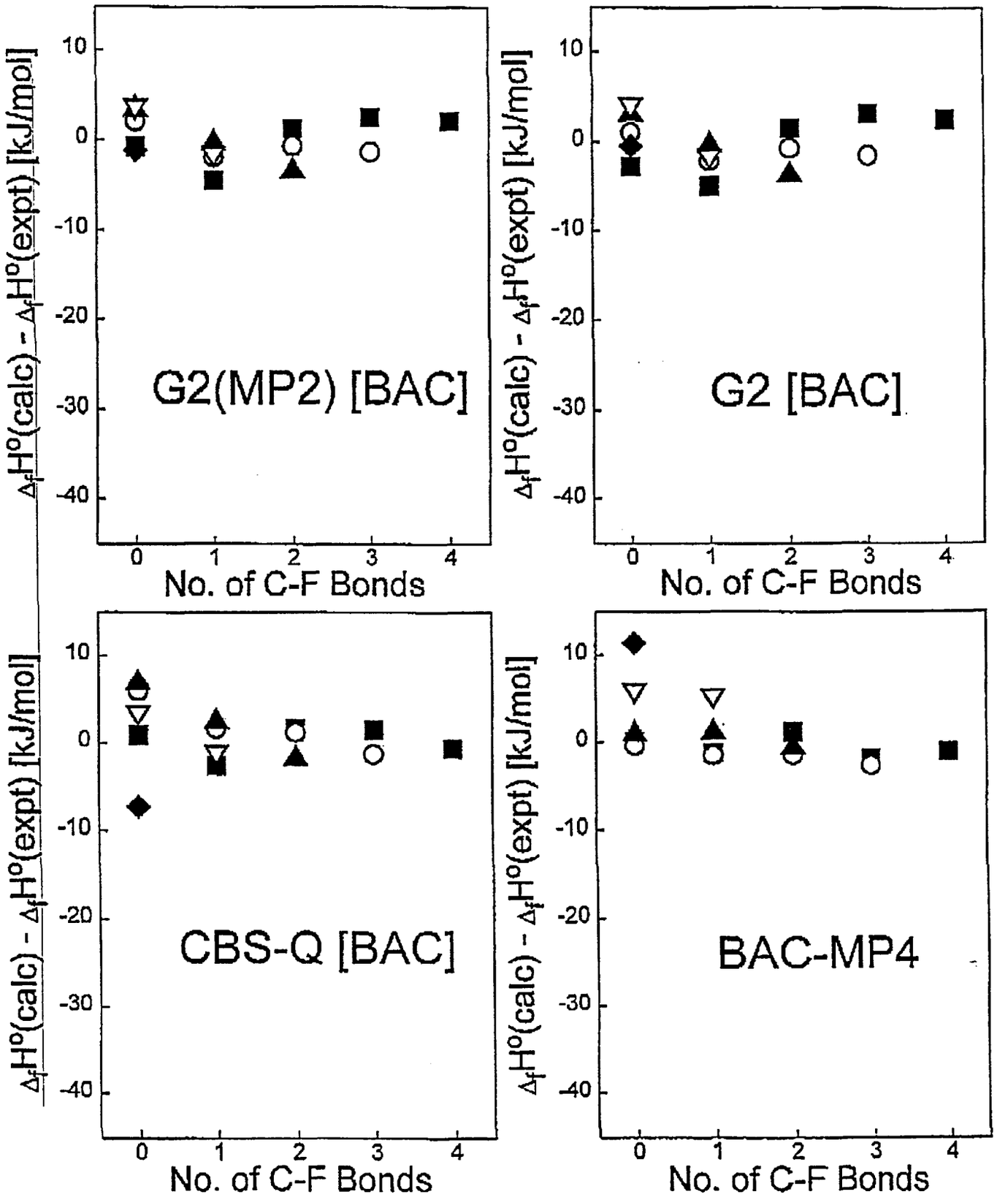

Figure 3: Deviation from Experiment of Formation Enthalpies for Fluoroethanes.

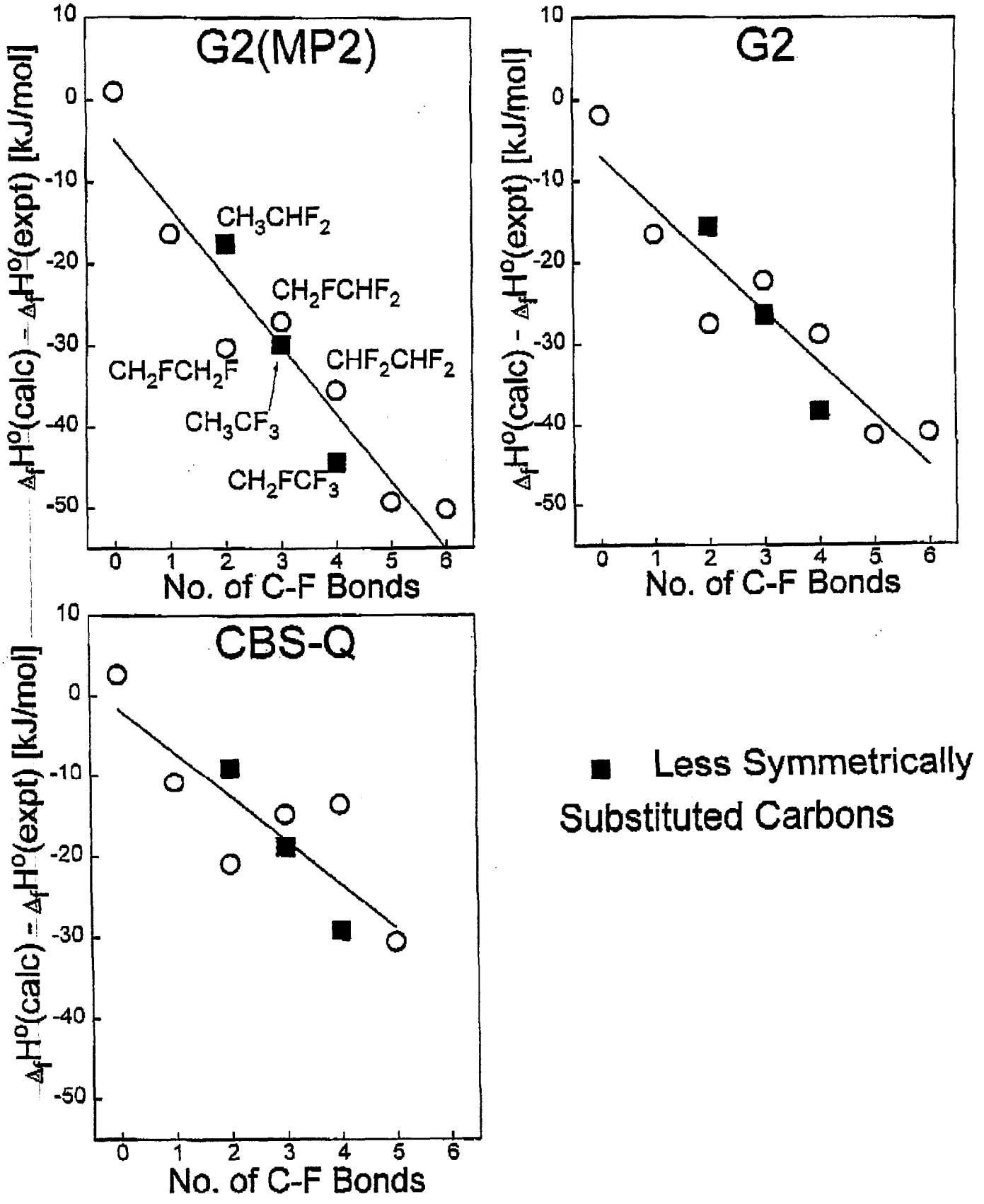

Figure 4: Deviation from Experiment of Corrected Formation Enthalpies for Fluoroethanes.

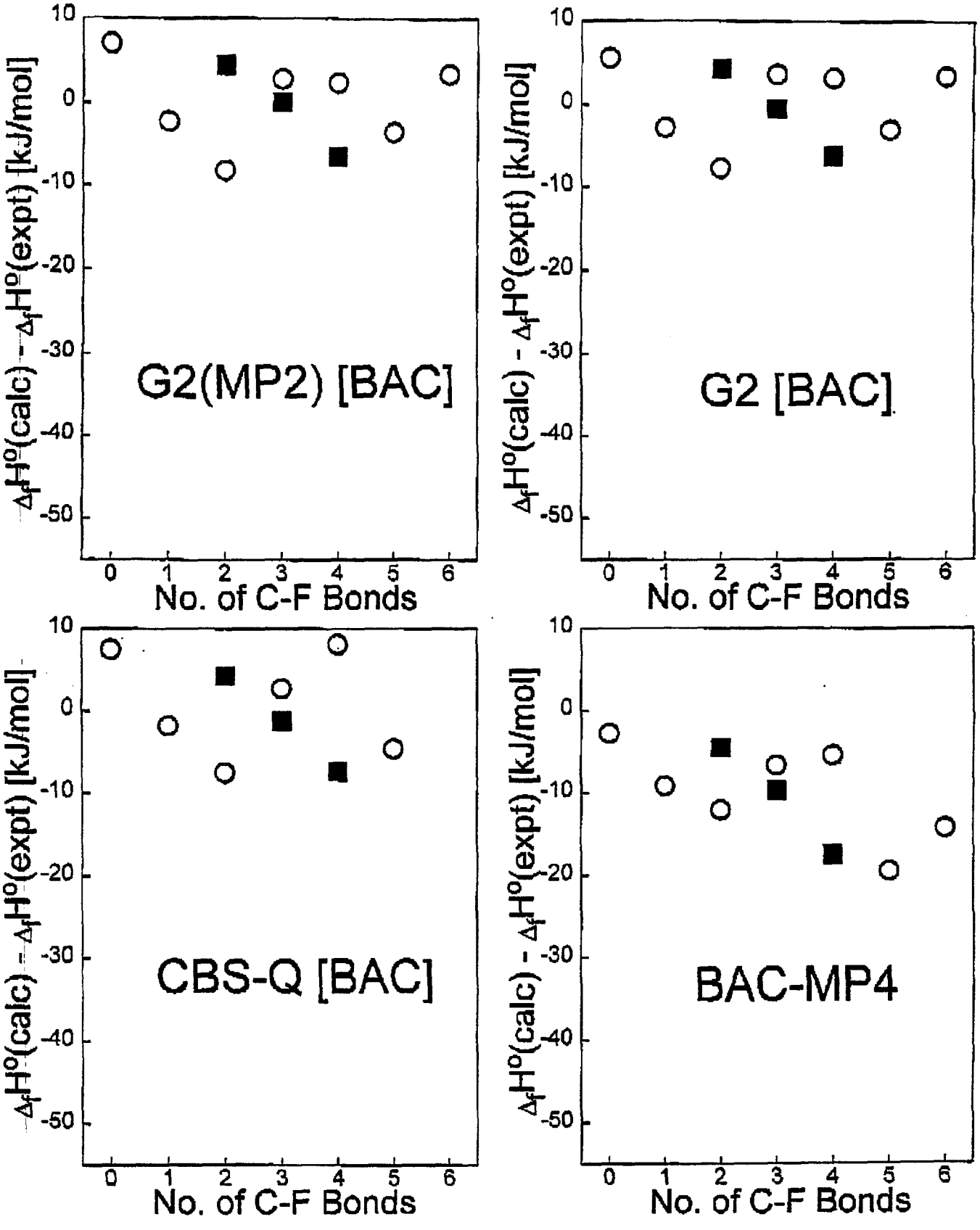

Figure 5: G2(MP2) reaction coordinate for

$CHFCl\text{-}CF_3 + OH \rightarrow CFCl\text{-}CF_3 + H_2O$

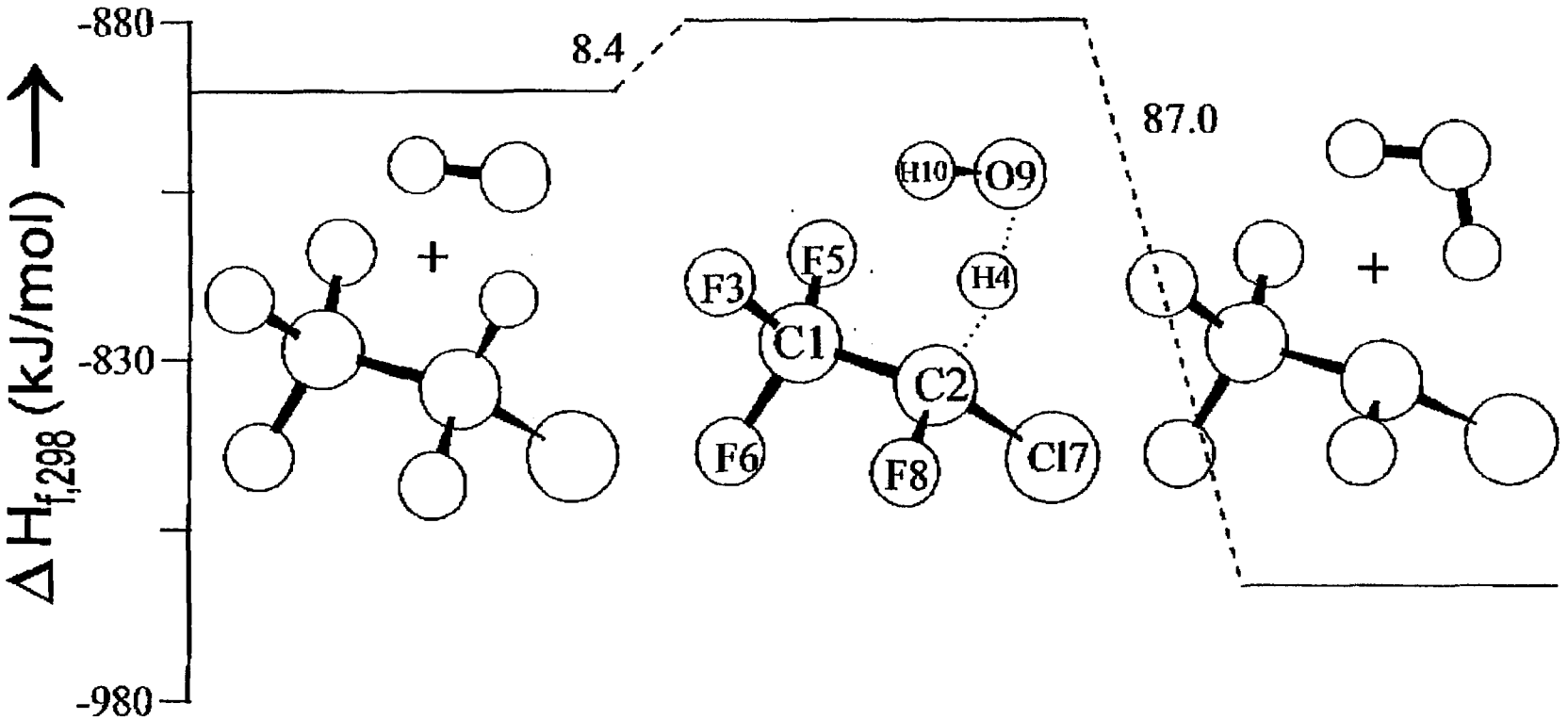

Figure 6: HF/6-31G(d) potential energy scan for the transition state of $CHFCl\text{-}CF_3$ + OH represented as 3-D and contour plot.

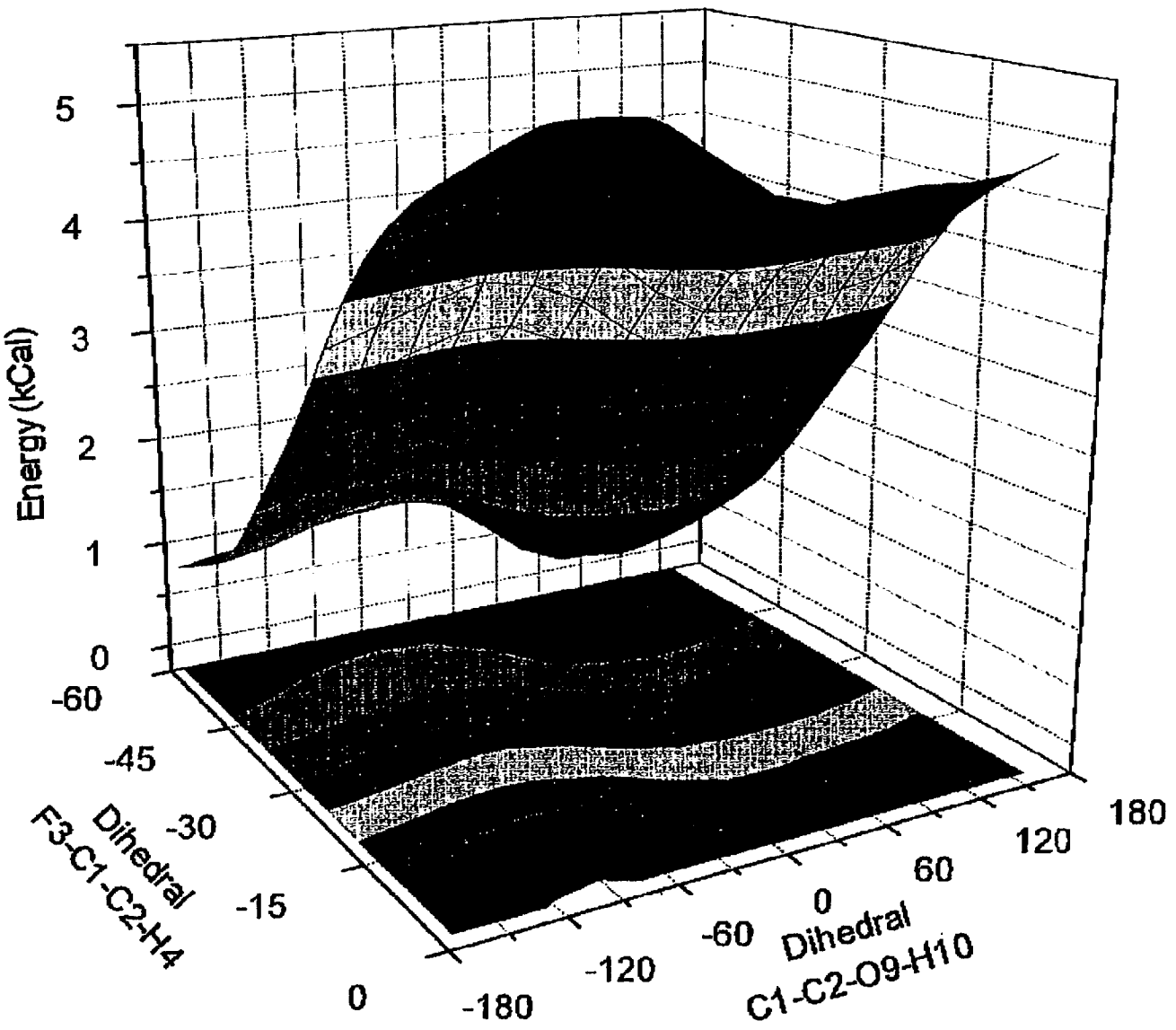

Figure 7: Comparison of the Calculated [G2(MP2)] vs. Experimental Arrhenius plot for the CHFCl-CF_3 + OH reaction.

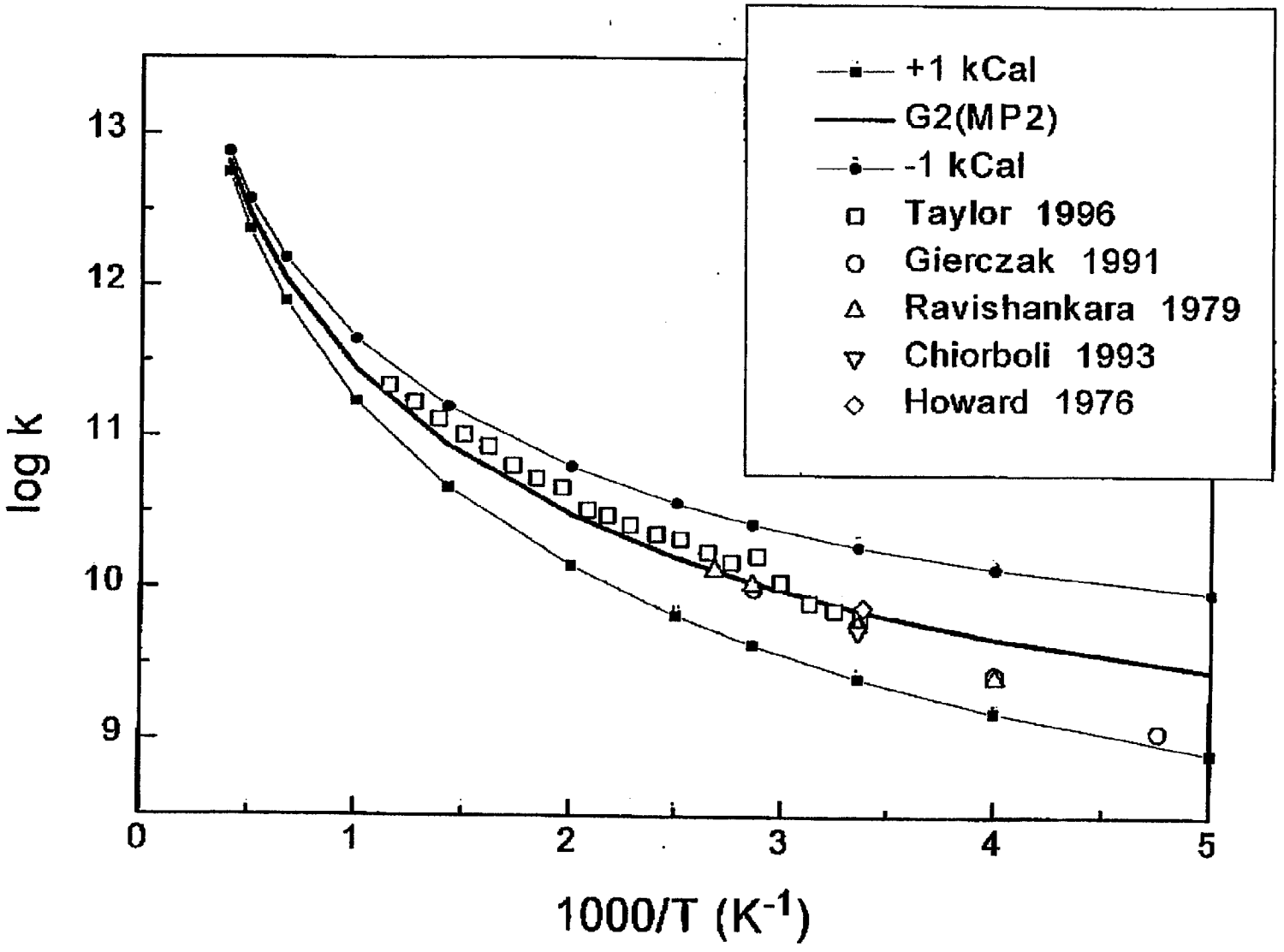

Figure 8: Rate Constants as a Function of Temperature for Abstraction of I and Abstraction of H by Hydrogen Radical.